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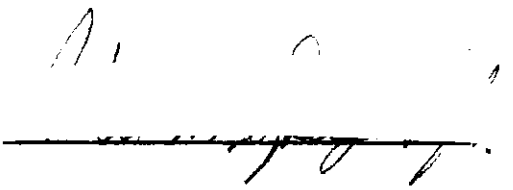

THE CHELOMETRIC TITRATION OF CADMIUM WITH AMPEROMETRIC END POINT DETECTION

A THESIS

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by

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WITH AMPEROMETRIC END POINT DETECTION

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SUMMARY

The subject of this investigation has been the application of the amperometric method to end-point detection in the titration of cadmium with ethylene-glycol-bis(aminoethyl)-tetraacetic acid (EGTA) in the presence of large excesses of zinc. The determination of cadmium in the presence of zinc has long been a difficult analytical problem. Recently Flaschka and Ganchoff introduced the use of ethylene-glycol-bis(aminoethyl)-tetraacetic acid (EGTA) to this problem. This reagent exhibits an unusual difference in the stabilities of its chelates with the two cations. The strong preference of this chelon for cadmium allows the titration of this cation in the presence of zinc. In the original method, a photometric end point is employed which is impaired by the presence of metals which precipitate at the high pH of the determination. The purpose of this investigation was to develop a method of end-point detection which would not be blocked by the presence of these precipitates. The amperometric method was found ideally suited for this purpose. The limitation on the method in the presence of precipitates is the point where co-precipitation becomes important. Titrating cadmium with ethylene-glycol-bis(aminoethyl)-tetraacetic acid by the use of an amperometric end point has been found in this respect complementary to the photometric method. The choice of method for a particular determination is controlled by the type and concentrations of potential interferences.

Cadmium has been titrated amperometrically with ethylene-glycol-bis(aminoethyl)-tetraacetic acid (EGTA) in the presence of zinc. Three

modifications for the titration are reported. Cadmium may be used to follow the titration at -0.90 or -0.70 volts versus the saturated calomel electrode in ammoniacal or acetate buffered medium respectively. The titration may also be performed in ammonia solution at -0.30 volts versus the saturated calomel electrode using copper as the amperometric indicator. The influence of iron, aluminum, magnesium, the alkaline earths, and lead was studied. Masking of iron by ascorbic acid was employed. Ascorbic acid was also studied as an effective remover of oxygen. At high ammonia concentration calcium and cadmium were determined successively, cadmium serving as amperometric indicator for the calcium determination. Representative data show that under appropriate conditions cadmium can be titrated in the presence of 500-fold the amount of zinc. Accuracy and precision are approximately 0.002 to 0.003 ml of a 0.1 M titrant solution.

CHAPTER I

INTRODUCTION

The ultimate purpose of this work is to establish a chelometric titration with amperometric end point detection for the determination of cadmium in the presence of zinc. A photometric determination has been described (1) in which cadmium is titrated with ethyleneglycol-bis-(aminoethyl)-tetraacetic acid (EGTA) in an ammonia-ammonium chloride buffer of pH 10. At this high pH many cations which do not form ammonia complexes are precipitated as hydroxides (iron and aluminum) and interfere with a photometric procedure. It is desirable to have a method which will not be hampered by the presence of a precipitate. The amperometric method is, however, limited by the presence of species which are reduced at the potential used to reduce cadmium during the determination. The new method here developed is complementary to the existing photometric method.

Titrations based on the measurement of polarographic diffusion currents were first performed by Heyrovsky and Berezicky (2) in 1929, although the method was proposed as early as 1897 by Saloman (3). Some years after the work of Heyrovsky, Major (4) simplified the method by measuring diffusion currents at a fixed applied potential rather than recording a series of polarograms after successive additions of titrant. Early developments of the method were concerned primarily with precipitation and oxidation-reduction systems. More recently applications have been made to chelometric titrations.

Cadmium is particularly well suited to polarographic studies. It gives a well defined, reversible wave in a wide variety of supporting electrolytes and over a wide pH range. This nearly ideal behavior has contributed to the ready development of a number of amperometric determinations of cadmium. The majority of the determinations developed to date involve the precipitation of the cadmium by an organic complexing reagent. Stock (5) used 8-hydroxyquinoline to titrate solutions from 0.75 to 2.5×10^{-3} molar in cadmium in an acetate buffer of pH 6. An applied potential of -0.9 volts vs. the saturated calomel electrode (SCE) was used. The selectivity of the method is extremely poor, since the reagent gives precipitates with almost all metals except the alkali metals. It is impossible to extend this method to lower concentrations of cadmium, due to the appreciable solubility of cadmium oxinate. A more suitable method employs 1,3-naphthioquinoline in 0.5 N H_2SO_4 plus 1 M KI at an applied potential of -0.9 volts vs SCE (6). Ammonium, magnesium(II), calcium(II), chromium(III), aluminum(III), titanium(IV), cobalt(II), nickel(II), manganese(II), and iron(II) ions do not interfere. The important advantage of this method is that zinc in large excess does not interfere if the acid and iodide concentrations are kept low. Silver, mercury, lead, copper, bismuth and antimony interfere and must be removed by precipitating from a hot solution onto an iron wire. Iron(III) must be removed since it destroys the iodide. The method is limited to solution of about 1 - 20 millimolar in cadmium. In a similar titration diantipyrinylmethane has been used (7) to precipitate cadmium from H_2SO_4 solutions containing the bromide complex. One to twenty millimolar cadmium can be determined in the presence of zinc(II), nickel(II), aluminum(III), and iron(II) in

200, 400, 60, and 200 fold quantities respectively. However, strict requirements are placed on the acid, chloride and bromide concentrations, and increased alcohol concentrations are known to affect the results. The amperometric titration is carried out at an applied potential of -0.8 volts vs SCE. In another method of comparable selectivity cadmium is titrated with iodide in the presence of a five or ten-fold excess of pyramidon (aminopyrine) at pH 2-5 (8). A "too great excess" of pyramidon gives low results. However, the titration can be followed amperometrically and "fairly large amounts of zinc, manganese, nickel, cobalt, ammonium, sulfate, nitrate, acetate and tartrate ions do not affect the results."

Other organic precipitants have been employed in less selective titrations of cadmium. Mercaptobenzothiazole dissolved in ethyl alcohol or aqueous alkali has been used to titrate cadmium in an acetate buffer of pH 3 - 6 at an applied potential of -0.8 to -1.0 volts vs SCE (9). Two moles of reagent are required forming $(C_7H_4NS_2)_2$ Cd. Both silver and copper interfere. Zinc is cotitrated. Sodium anthranilate has been used as an organic precipitating reagent at pH 5.5 (10). Anthranilates, bromoanthranilates, and pyridins have also been used in conjunction with NH_4CNS to give precipitates of the type $Cd(py)_2(SCN)_2$ (11). These methods are subject to interferences by iron, zinc, nickel, cobalt, manganese, lead, mercury(II) and copper, all of which form precipitates with anthranilates. BAL (2,3-dimercapto-proponal) (12) and 2-nitro-1-hydroxy-4-benzene arsonic acid (13) have also been used as unselective organic precipitants in amperometric titrations of cadmium. Diethyldithiocarbamate

is also an unselective precipitant for cadmium and zinc. The lack of selectivity of this reagent has been overcome by extraction techniques, followed by an amperometric titration with diethyldithiocarbamate of the isolated metals. Zinc and cadmium are separated from bismuth, iron, copper, nickel and cobalt by extraction from an ethyl acetate solution of the diethyldithiocarbamates with 1 N hydrochloric acid. Cadmium diethyldithiocarbamate is then precipitated in strong ammonia in which the zinc compound is soluble (14).

Several amperometric titrations based on ferrocyanide have been suggested. Ramaiah and Agarwel (15) investigated the composition of the cadmium ferrocyanide complex polarographically in KCl, KBr, KNO, KNO_3, $(NH_4)_2SO_4$, K_2SO_4 and NH_4Cl. They found a complex precipitate of composition $Cd_5K_6[Fe(CN)_6]_4$ and suggested an amperometric titration could be performed with errors of about one per cent. Saraswat (16) determined cadmium amperometrically with ferrocyanide in citrate solution with a reported experimental accuracy of 0.5 per cent. Kao and Chuang (17) found a precipitate of the composition $(NH_4)_6Cd_5[Fe(CN)_6]_4$ from 1 N HCl containing ammonium sulfate. Basinske and Kuik (18) found complexes of the composition $Cd_2Fe(CN)_6$ in Li_2SO_4; they were able to titrate cadmium with $Li_4Fe(CN)_6$ with an error of less than two per cent in 5×10^{-4} to 1×10^{-2} Molar solutions. Kalvoda and Zyka (19) described the conditions for titration of cadmium and zinc in the presence of lead, aluminum, magnesium, calcium, strontium and barium with 0.1 molar $K_3Fe(CN)_6$. All of these procedures are quite empirical in practical application. The composition of the precipitate produced has been shown to be a more or less

continuous function of temperature, presence of other salts, acidity, stirring, concentrations of reagent, and even appears to be influenced by the method of end-point detection. Interferences also plague this method. Iron, manganese, copper, nickel, arsenic, cobalt, antimony, silver, aluminum and zinc are known to interfere. This precipitation titration, as well as the others mentioned above, are subject to erratic behavior, due to coprecipitation and absorption and to the frequent time dependences associated with precipitation titrations in general, plus the likelihood of interference at the drop surface.

Application of chelometric procedures to amperometric titrations has greatly expanded their range of usefulness as well as providing a route around many of the disadvantages of precipitation titrations. Most chelons are quite soluble in water and show no tendency to decompose. They combine rapidly with large numbers of metal cations to form soluble complexes which dissociate only slightly. Most important to polarographic applications, however, chelons in general are inactive at the dropping mercury electrode and the complexes formed are reduced at a much more negative applied potential than the solvated cations. Three different approaches have been used in chelometric amperometric titrations. These are discussed in Chapter II. Chelometric titration with amperometric end-point detection has been applied to the determination of cadmium by Pribil and Matyska (20) and by Nikelly and Cooke (21).

CHAPTER II

THEORY

The usefulness of amperometric titration is greatly expanded by the use of chelons. Many of the restrictions of precipitating reagents are circumvented by the use of chelons, but other restrictions are imposed on the system. The latter, however, are generally less serious. In general, the following conditions must be met for the successful amperometric titration of an element with a chelon:

(a) The given cation must form a stable complex sufficiently rapidly.
(b) No elements reducible at a more positive potential must be present.
(c) The accompanying elements must form, under the conditions of the determination, less stable complexes than the element determined. (20)*

A few simple calculations are an invaluable guide in evaluating the conditions necessary for a successful titration. The discussion to follow will indicate the foundations of the calculations necessary for an evaluation of conditions b and c, above. The conditions of rapid reaction, expressed by a above, can usually be established only by direct observation of the system under investigation.

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* It should be noted that certain of these restrictions may be relaxed at times. In particular, elements reducible at more positive potentials may be present.

Conditional Constants

In evaluating the conditions for a determination, the primary concern is the extent to which the reaction between the element to be determined and the titrant proceeds. The reaction may be written

$$M + Y \rightleftarrows MY \qquad (1)$$

where M is the metal ion and Y the chelate ligand.* For this reaction an equilibrium constant may be written

$$K_{MY} = \frac{[MY]}{[M]\,[Y]} \qquad (2)$$

The analytical chemist expresses equilibrium constants in terms of concentrations. The concept of activities, an annoying intrusion into his equations, can usually be omitted, although it must not be ignored. In most instances, stability constants are measured as concentration constants at a specified ionic strength. By appreciating the conditions of this determination and the magnitude of the change of the constant with ionic strength considerations can be readily made. Ringbom (24) has shown that activities can be ignored in practice by the analytical chemist in the range between $\mu = 0.1$ and 0.5 for most ions. In this range the stability constants are not sensitive to changes in ionic strength and, if measured in this range, as most are, may be taken as constant with regard to ionic strength. Throughout this work ionic strength was kept reasonably constant. No further mention of ionic

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* Charges will be omitted unless their presence is required for the sake of clarity.

strength will be made.

The constant defined in equation 2 is the absolute* equilibrium constant. The concentration terms involved in this expression are the concentrations of the free species. Thus, [M] is the concentration of the free metal ion, [Y] is the concentration of the completely ionized anion of the chelon, and [MY] is the concentration of the free complex. In practice, it is necessary to consider competing equilibria due to solvent, buffers and impurities. The scheme shown below aids in visualizing the competitions involved.

$$M^{+2} + Y^{-4} \longrightarrow MY^{-2} \qquad (3)$$

$$\begin{array}{ccccccccccccc} + & & + & & + & & + & & + & & + & & + \\ OH^- & & pZ & & nH^+ & & N^{+2} & & H^+ & & OH^- & & X \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ MOH^+ & & MZ_p^{+2} & & H_nY^{n-4} & & NY^{-2} & & MHY^- & & MOHY^{-3} & & MXY^{-2} \end{array}$$

M^{+2} is the bivalent metal ion to be titrated, Y^{-4} is the chelon (titrant), MY^{-2} is the chelonate, Z is a foreign complex former, N^{+2} is an interfering metal ion, and MHY^-, $MOHY^{-3}$, MXY^{-2} are mixed complexes with H, OH, and X in the scheme. Schwarzenbach (23) has studied the effects of certain of these side reactions and has defined the apparent stability constant in order that the theory of complexometric titrations might include their effects. This constant reflects the effect of the pH on the

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* Convention in chelometric theory establishes the use of term "absolute constant" to refer to a concentration constant, with the realization that this constant is not equivalent to the thermodynamic absolute constant.

equilibrium by protonation of the free chelon. It also reflects the effects on the equilibrium of the buffer components, as well as any accessory complexing agents. Ringbom (24,25) extended this approach to include side reactions involving the formation of hydroxo or acid metal chelates and metal hydroxides. He has also shown how the presence of competing ligands and metals are reflected in the "conditional constant." This term was introduced by Ringbom at the suggestion of I. M. Kolthoff to emphasize the dependence of the constant on the conditions under which it is observed. The connotation is the same as the term "apparent stability constant." The expression "effective" stability constant is also used.

The conditional stability constant for the reaction (3) is defined by the equation

$$K_{eff} = \frac{[MY']}{[M'].[Y']} \qquad (4)$$

where $[M']$ and $[Y']$ denote the concentration of metal and ligand not involved in the formation of MY, while $[MY']$ denotes the concentration of MY not involved in proton, hydroxo, or other complexes. Once the values of the primed species have been determined the conditional constant can be used just as any stability constant.

To facilitate the calculation of the apparently abstract concentration of uncomplexed ions, Schwarzenbach has introduced the coefficients which are now in common usage. The α-coefficient is

defined as:

$$(a)\ \alpha_M = \frac{[M']}{[M]} \qquad (b)\ \alpha_Y = \frac{[Y']}{[Y]} \qquad (c)\ \alpha_{MY} = \frac{[MY']}{[MY]} \tag{5}$$

Knowledge of the α-coefficients under given conditions provides an easy calculation of the effective constant from the absolute stability constant, as:

$$K_{eff} = \frac{\alpha_{MY}}{\alpha_M \alpha_Y} K_{MY} \tag{6}$$

It may be seen from the above that the coefficients are a measure of the extent of the side reactions. If M reacts only with Y to form MY, α_M is seen to be one. Any other reactions of M increase the amount of M not combined in MY and thus the value of $[M']$. Thus α_M takes on a value greater than one which reflects a lower value of the conditional stability constant. Similarly, α_Y and α_{MY} reflect side reactions involving Y and MY. As expected, alpha is a function of the equilibrium constant of the side reaction, and from a knowledge of this constant alpha may be calculated for given conditions. The side reactions indicated in equation 3 between chelon and n protons are particularly important. The stability constants of the proton complexes are defined by the following expressions:

$$(a)\ K_1 = \frac{[HY]}{[H]\,[Y]} \qquad (b)\ K_2 = \frac{[H_2Y]}{[H]\,[HY]} \qquad (n)\ K_n = \frac{[H_nY]}{[H]\,[H_{n-1}Y]} \tag{7}$$

At any pH the unmetallized chelon exists in solution in several forms. The total concentration [Y'] may be expressed as the sum of the several forms

$$[Y'] = [Y] + [HY] + [H_2Y] + [H_3Y] \ldots\ldots\ldots [H_nY] \tag{8}$$

By application of the expressions of equations 7a, b, c, ...n, we find

$$(a)\ [Y'] = [Y] + K[H][Y] + K_1K_2[H]^2[Y] \ldots . K_1 \ldots . K_n[H][Y] \tag{9}$$

$$(b)\ [Y'] = [Y]\left[1 + \sum_{i=0}^{n} \bar{K}_i[H]^i\right] \text{ where } \bar{K}_i = \prod_{i=0}^{n} K_i$$

$$(c)\ [Y'] = [Y]\alpha_Y \text{ where } \alpha_Y = \sum_{i=0}^{n} \bar{K}_i[H]^i \qquad K_0 = 1$$

The pH-dependent term (see Figure 1) is just that previously defined and can be used to judge the effect of the proton side reaction on the metal-chelon equilibria.

Influence of a Second Metal

The effect of a second metal, as N in equation 3, is similar to that of protons. In this case, the stability constants of the metal constants of the metal replace the proton stability constants and pM(-log [M]) replaces pH.

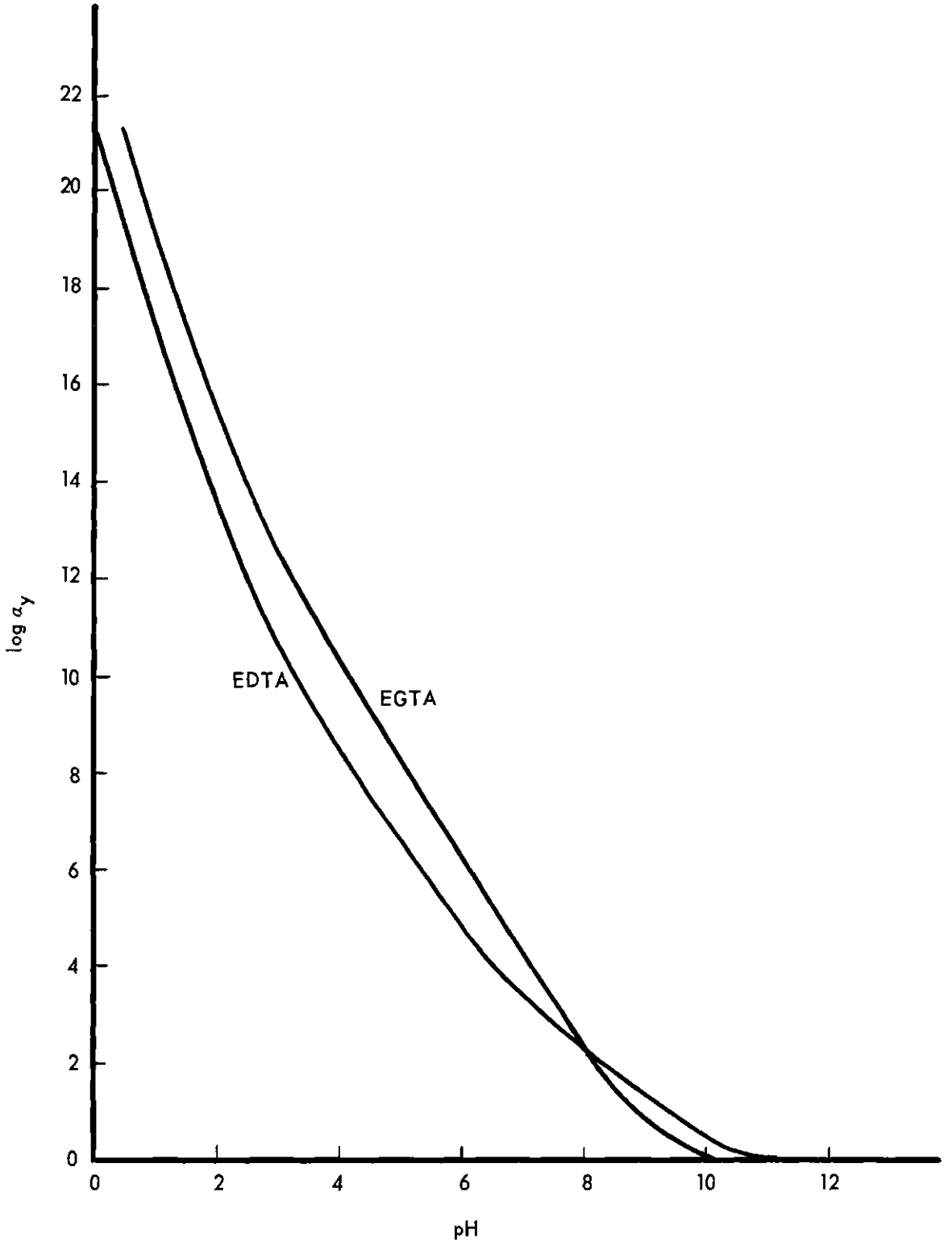

Figure 1. Logarithm of α_y as a Function of pH for EDTA and EGTA.

Influence of a Second Complex Former

When a second complex former is present, as Z in equation 3 the metal ion is distributed between the two ligands. The conditional stability constant which accounts for the influence of Z is given by

$$K_{M'} = \frac{[MY]}{[MY'] \cdot [Y]} \tag{10}$$

and from equation 7,

$$K_{M'} = \frac{[MY]}{[M] \cdot [Y]\alpha_M} = K_{MY} / \alpha_{M'} \tag{11}$$

The coefficient α_M can be calculated in a manner similar to that shown for α_Y. We find

$$\alpha_M = \sum_{i=0}^{q} \left[\prod_{i=0}^{q} K_i \; [Z]^i \right] \tag{12}$$

where K_i is the stepwise stability constant for M_iZ. Ammonia is a complex former which is frequently present as a competing ligand. Alpha-coefficients is a function of pH in ammonial media. Figure 2b shows these coefficients as a function of ammonia concentration (23).

Influence of Several Simultaneous Competing Side Reactions

In practice almost every system involves consideration of more than one of the competing side reactions of equation 3. For these cases overall coefficients can be calculated as the sums of the individual coefficients by the use of the equations:

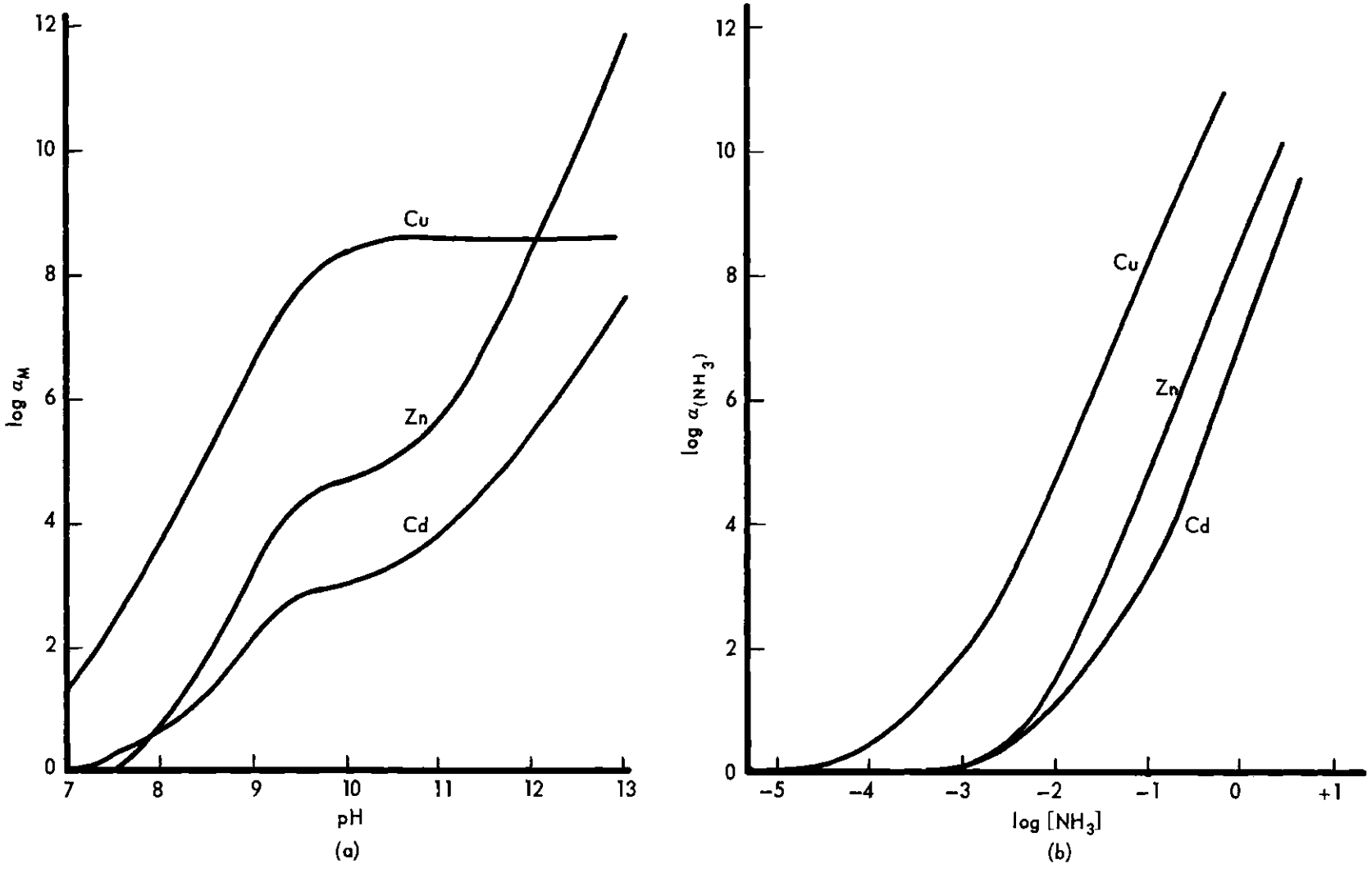

Figure 2. Alpha Coefficients for Various Metals as a Function of
a. pH in 0.1 M Ammonia
b. Ammonia Concentration.

$$\alpha_{MY} = \alpha_{MY(X_1)} + \alpha_{MY(X_2)} + \ldots \alpha_{MY(X_n)} + (1-n) \quad (13)$$

$$\alpha_{M} = \alpha_{M(Z_1)} + \alpha_{M(Z_2)} + \ldots \alpha_{M(Z_n)} + (1-n) \quad (14)$$

$$\alpha_{Y} = \alpha_{Y(H)} + \alpha_{Y(N_1)} + \ldots \alpha_{Y(N_n)} + (1-n) \quad (15)$$

where n is the total number of interfering components. Often one of the alpha terms will predominate and the others may be ignored, indicating that only one of the side reactions is proceeding to a significant extent.

Voltametric Methods

Polarographic Methods

If an electro-reducible* substance is reduced at a dropping mercury or rotating platinum electrode, a plot of the reduction current versus applied voltage will exhibit, at sufficiently negative potential, a plateau (Figure 3a). This plateau is a result of the limitation imposed on the current flow by the rate of diffusion of the reducible substance to the electrode surface. As the reducible substance is removed from the surface of the electrode by, for example, reduction and amalgamation, a concentration gradient is established extending from the surface. The concentration gradient is related to the current intensity (i) by the Ilkovic equation** for a dropping mercury electrode (DME):

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* Oxidation processes can be treated in an analogous manner. They are here omitted for the sake of brevity.

** Derivations of the Ilkovic equation are available in most polarographic monographs.

$$i = 607\ D^{1/2}\ m^{2/3}\ t^{1/6}\ n(C_{red} - C^{o}_{red}) \qquad (16)$$

through the polarographic diffusion coefficient whose value depends on the concentration gradient. In the Ilkovic equation D is the polarographic diffusion coefficient; m is the mass of the mercury drop electrode; t is the drop time in seconds; and n is the number of electrons in the electrode process. The constant 607 is derived from geometric considerations to allow for a non-spherical mercury drop electrode and for the growth of the drop. It also includes the Faraday constant. The concentration terms apply to the extremes of the gradient of the reducible substance C_{red} being the concentration in the bulk of the solution and C^{o}_{red} that at the electrode surface. As C^{o}_{red} approaches zero, the rate of diffusion becomes proportional to the concentration in the bulk of the solution and the limitingcurrent is reached. The rate of diffusion and thus the current level maintained by diffusion, is directly proportional to the concentration of the reducible substance. It is this fact which forms the basis for polarographic measurements (26). This limiting current is in fact the sum of the contributions of all mechanisms by which current flows through the solution. Two mechanisms other than that of the diffusion current are important. These give rise to the residual current and the migration current. The residual current is the sum of the current required to charge the electrode - the capacitor current - plus a small current resulting from accidental impurities. The migration current is the current due to the migration of ions under the influence of the electrostatic forces between electrode and ion. The effect of the migration current can be lessened by the addition of relatively large concentrations of a supporting electrolyte, so that the relative currents carried

by the other ions are reduced to a negligible value.

Although direct calculation of concentration from diffusion current is possible, this approach is seldom practical. The impracticallity of direct calculation arises from the large numbers of factors, the exact values of which must be known absolutely. Because the diffusion current is proportional to $m^{2/3}\ t^{1/6}$, any change in these factors will cause corresponding changes of the diffusion current. The capillary characteristics are in turn affected by several variables, three of which are of primary concern. These are: 1) The effective mercury pressure at the drop - that is, the mercury pressure corrected for the back pressure of the solution; 2) The potential of the mercury electrode; and 3) The temperature, since the density and the viscosity of mercury change with temperature and therefore m and t do, the magnitude of the change in current being about 0.2 per cent per degree. So the capillary characteristics must be known and the factors which change them must be carefully controlled, or corrections must be made. The absolute value of the diffusion coefficient must be known and account must be made for the dependence of the coefficient on the temperature and the ionic strength. The currents arising from substances reduced at more positive potentials* must also be be known, since their reduction at the electrode introduces a background current. These are only a few of the variables which enter into a direct polarographic determination of concentration. Further problems are

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* In polarography the dropping mercury is usually used as the cathode and is assigned a negative potential with respect to a standard reference electrode which is generally a saturated calomel electrode. "Higher potential" refers to a more negative potential of the dropping mercury electrode.

introduced by the presence of surface active agents (maximum suppressors), tilting of the capillary, and variations in solvent composition.

The potential at which an electro-reducible substance is reversibly reduced is conventionally expressed in the form of a half-wave potential, $E_{1/2}$. That is the potential at which the diffusion current reaches one half of its plateau value. Lingane has shown that the half-wave potential at a dropping mercury electrode is related in a simple way to the ordinary standard potential of a metal, its solubility in mercury, and its affinity for mercury (31). It has been further shown that the half-wave potential of a complex, such as a metal chelate, is "shifted" to a more negative potential than that of the simple metal by an amount which depends on the stability constant of the complex K_c, and the concentration of the complexing agent, C_Y. This relationship is shown by equation (17).

$$E_{1/2)_c} = E_{1/2)_s} - \frac{0.0591}{n} \log K_c - \frac{0.0591p}{n} \log C_Y \qquad (17)$$

where $E_{1/2)_s}$ and $E_{1/2)_c}$ are the half-wave potentials for the simple and complexed metal; n is the number of electrons involved in the electrode process; and p is the number of complexing ligands per metal ion (26).

Amperometric Titrations

Many of the difficulties of direct polarograph measurement can be avoided by following the decrease of the diffusion current, at constant potential, of the electro-active substance while reducing its concentration by titration. The titration curve, which is a plot of diffusion current versus titrant added, ideally consists of two straight lines of different slopes whose intersection corresponds to the end point.

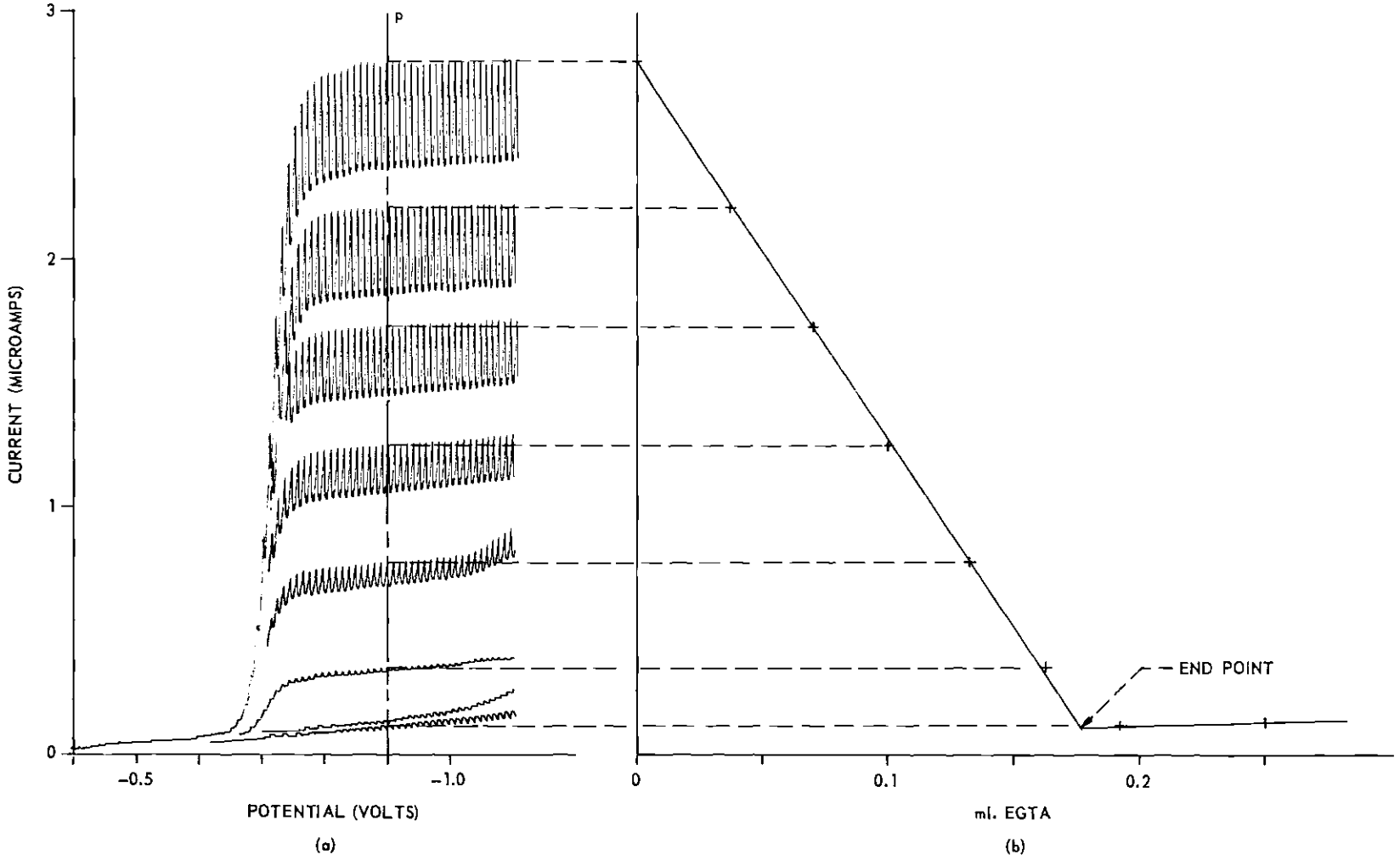

Figure 3. Relationship of Amperometric Titration to Polarographic Method
a. Polarograms of Cadmium in Buffer 10
b. Amperometric Titration of Cadmium in Buffer 10 with EGTA at potential p.

Such a titration is called an amperometric titration. Figure 3 demonstrates the relationship between polarograms recorded after successive addition of titrant and the amperometric titration curve. The potential p is the constant potential at which the amperometric titration is performed.

Amperometric titrations are inherently more accurate than the direct polarographic method. They require no knowledge of temperature or capillary characteristics; the only condition is that these remain constant throughout one titration. Since amperometric titrations involve only the difference in currents, the measured currents need not be converted to absolute values, thus calibration of the current-measuring system is unnecessary. The constant potential employed allows the apparatus for amperometric titrations to be very simple.

In a polarographic determination the residual current must be estimated by interpolation, as shown in Figure 3a, or determined separately in a solution hopefully identical to the sample solution with the exception of the titrated specie. In the amperometric method the residual current is not important. In addition, each branch of the titration curve is effectively the average of the recorded points. Thus, random errors are eliminated to a very high degree.

Amperometric titrations frequently possess greater sensitivity and wider applicability than either conductometric or potentiometric methods. In fact, the method is extremely well suited to precise determinations of trace quantities. Concentrations of 10^{-2} to 10^{-5} molar can be measured and in favorable cases the range can be extended to micro-molar concentrations. Applications of amperometric methods

are much more general, extending even to species which show no activity at the indicator electrode. In such cases, an electro-active titrant can frequently be used.

An important group of amperometric titrations has been devoted to the investigation of the use of organic reagents as volumetric reagents. Although early developments were concerned primarily with precipitation methods, more recently, application has been made to chelometric titrations. Three different approaches have been used in chelometric titrations. In the first, the diffusion current due to the titrated substance is followed directly. This method is illustrated in Figure 3. Alternatively, the diffusion current resulting from the reduction of an indicator ion is followed through the titration (27). This has been called the amperometric indicator method. The ion chosen must be reducible at a more positive potential and form complexes which are less stable than the ion being titrated. Under these conditions the concentration of the indicator will not be effected by addition of titrant so long as some of the titrated specie remains. After the end point, addition of more complexing agent will decrease the indicator concentration and thus its diffusion current. This drop in current indicates the end point (Figure 4). This method is ideally applied to cases where conditions for the direct titration are impractical or do not exist. In fact, this method can often be used to determine polarographically inactive substances.

The third approach is based on the appearance of an "anodic wave for the free chelon after the end point." (28). The electrode reaction for the "free chelon" wave may be written

$$Hg^{o} + H_{n}Y^{n-4} \rightarrow HgY^{n-2} + nH^{+} + 2e^{-}$$

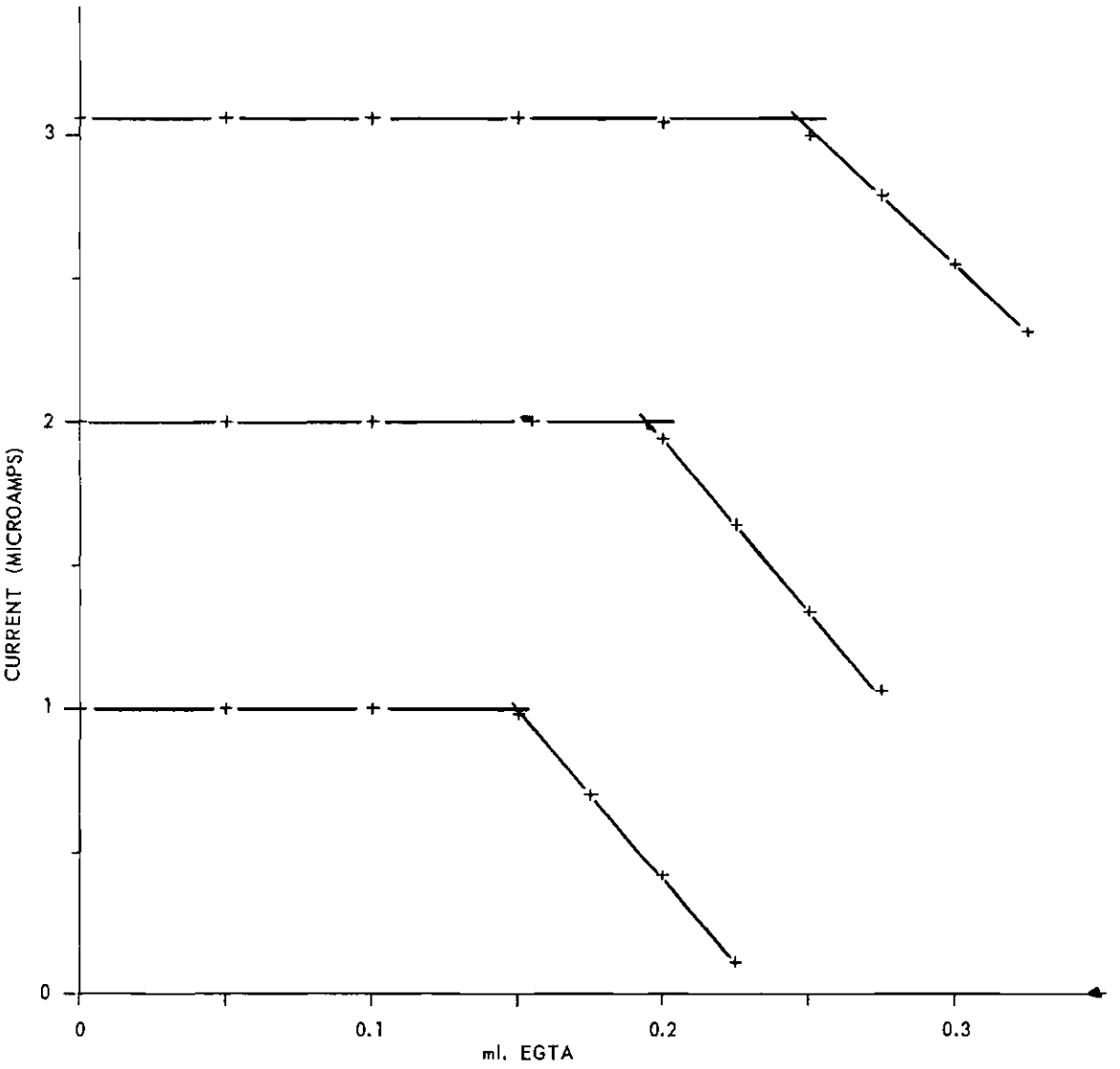

Figure 4. Amperometric Titration of Cadmium with EGTA, using Copper as as Amperometric Indicator at -0.30 volts.

The term "free chelon" wave should not be taken to indicate that the chelon is involved directly in the electrode reaction. The electrode reaction is the two-electron oxidation of mercury. The presence of the chelon serves as a driving force for the reaction by removing the oxidation product Hg^{+2}. This driving force reduces (shifts to less positive values) the electrode potential necessary to oxidize mercury. The magnitude of the anodic current at the reduced potential depends on the diffusion of chelon to the electrode surface, and thus on the concentration of free chelon in the bulk of the solution. This reaction occurs only after all ions which complex with Y under the conditions of the titration are complexed. The advantage of this method arises from the fact that the chelon wave is detectable at low potentials where many normally interfering ions are inactive. Notable among the interferences avoided is the oxygen reduction wave. "Hence the time-consuming operation of removing oxygen from the solution before analysis and after the addition of each aliquot of titrant is eliminated." (28). An important disadvantage is the interference of halide ions. This becomes particularly critical in practical analysis where chloride is involved in the majority of the cases.

CHAPTER III

EQUIPMENT AND CHEMICALS

Instrumentation

During the course of this investigation two instruments were used. Preliminary work was done employing a Sargent Model III manual polarograph. This manual instrument was adapted for recording by using a constant rate motor to drive the voltage scan and a Sargent recorder to record current. The main body of the experimental work was performed on a Sargent Model XV recording polarograph. The use of such an instrument is by no means demanded by the method. The only advantage of a recording instrument is its versatility which is so important in initial investigations of a system. For routine analysis purposes a much more simple instrument will suffice.

Several cells were employed for titrations. The most generally useful was a 200 milliliter beaker equipped with a coarse-sintered glass bottom through which nitrogen could be passed. A stopcock was provided to control the gas flow. An attempt was made to provide a shield for the dropping mercury electrode so that continuous passage of nitrogen could be employed without interfering with current readings. It was found, however, that the shield so impeded the flow from the bulk of the solution, and thus to the neighborhood of the electrode, that no time was saved by continuous bubbling. A 100 milliliter beaker equipped with a sintered glass tube for admitting nitrogen was also used.

The cell assembly included the dropping mercury electrode, a

U-tube agar salt bridge, which provided contact with a Saturated Calomel Electrode (SCE), a glass electrode used in conjunction with the previously mentioned saturated calomel electrode for pH measurements, and a buret. Each component of the cell assembly was rigidly supported by suitable clamps, and was passed through a rubber stopper into the cell (Figure 5).

A Leeds and Northroup Model 7664 pH meter was used for all measurements of pH. The meter was standardized against a saturated solution of potassium acid tartrate - pH 3.57.

A variety of burets were employed, depending on the size of the sample determined. The most generally useful was a Sargent Model C automatic constant rate buret. Burette and pipette standardizations yielded negligible corrections.

The saturated calomel electrode was made by covering a mercury layer deep with a layer of a paste made by stirring equal weights of mercurous and potassium chlorides with a little saturated potassium chloride. The paste was then covered with a saturated solution of potassium chloride containing some additional solid. Electrical contact with the mercury was accomplished by means of a platinum wire sealed in a glass tube so as to project into the mercury.

Bacterological agar and reagent grade potassium chloride were used in the construction of the salt bridge. The agar gel was prepared by warming agar (4 gm) in water (90 ml) until the mixture was clear. Potassium chloride (30 gm) was then slowly added. The gel was then pipetted into a U-tube and allowed to stand undisturbed until it had solidified.

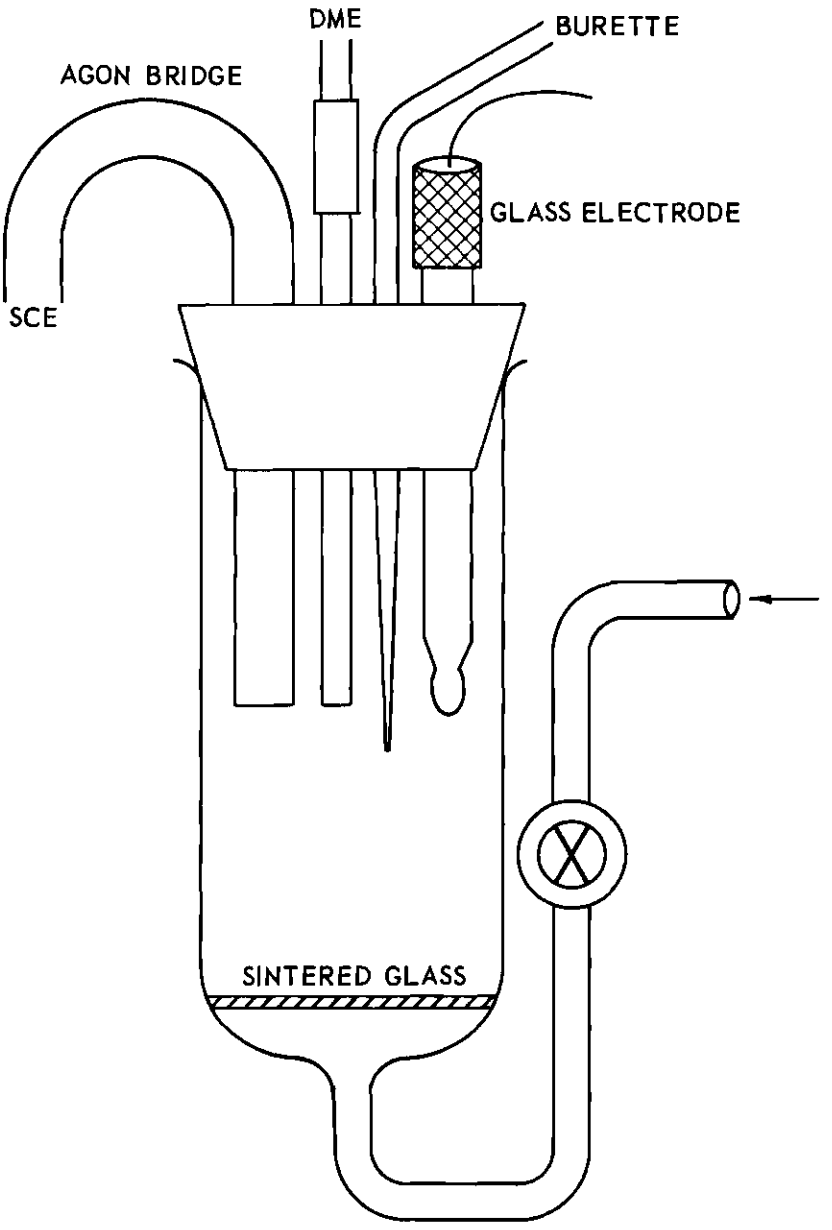

Figure 5. Titration Cell and Assembly.

Chemicals

Ethyleneglycol-bis(aminoethyl)-Tetraacetic Acid (EGTA)

EGTA from the G. F. Smith Company was used to prepare approximately 0.1 M solutions of the chelon. Dissolution was aided by the addition of small amounts of sodium hydroxide. The resulting solution was filtered and standardized against calcium chloride solution, prepared from reagent grade calcium carbonate. The indicator Calcon was used to detect the end point in a visual titration.

Disodium Ethylenediamine Tetraacetate, Dihydrate (EDTA)

Reagent grade EDTA (37.2 gm) was dissolved in de-ionized water (1 l), using a few drops of 50 per cent sodium hydroxide to hasten dissolution. The solution was prepared to be about 0.1 M and was standardized against a standard copper solution using Murexide indicator.

Lactic Acid

J. T. Baker 85 per cent lactic acid (9 ml) was diluted to one liter.

Tartrate Solution

Reagent grade solid tartaric acid (15.0 gm) was used to prepare one liter of an aqueous solution. Dissolution was aided by a small amount of sodium hydroxide.

L-Ascorbic Acid

Eastman Organic Chemicals reagent grade was used.

Copper Nitrate Solution

Reagent grade copper wire was cleaned, dried and accurately weighed to give 0.1000 M Solution. The wire (6.354 gm) was dissolved

in the minimum amount of nitric acid, the solution warmed to dispel nitrogen oxides and diluted to the mark (1 L.).

Calcium Chloride Solution

Reagent grade calcium carbonate (10.009 gm) was accurately weighed and dissolved in hydrochloric acid. The solution was boiled to dispel excess carbon dioxide, cooled, and diluted to one liter. This solution was used to standardize the EGTA solution.

Cadmium Nitrate Solution

Reagent grade cadmium nitrate (23.6 gm) was dissolved in one liter of de-ionized water. The solution was then standardized with EGTA, using a visual titration with Eriochrome Black T indicator.

Potassium Nitrate

Reagent grade potassium nitrate (101.10 gm) was dissolved in one liter of water to make a 1 molar solution.

Other Metal Salt Solutions

Reagent grade salts were used to prepare the aqueous solutions. For salts known to hydrolyze a few drops of nitric acid were added.

Triton X-100

Rohm and Haas Triton X-100 (0.2 ml) was warmed in de-ionized water (100 ml) to give a 0.2 volume per cent solution.

Antifoam 60

Enough General Electric Silicone Antifoam Emulsion "Antifoam 60" was dispersed in de-ionized water to make a 0.5 per cent solids emulsion.

Gelatine Solution

Bacterological gelatine (0.5 gm) was dissolved by warming in de-ionized water (100 ml) to make a 0.5 per cent stock solution a fresh

solution was prepared each day.

Buffer Solutions

Buffer pH 10

Reagent grade ammonium chloride and ammonium hydroxide were used to prepare the buffer. Ammonium chloride (140 gm) and ammonium hydroxide (1040 ml) were combined and diluted to two liters.

Acetate Buffer pH 5

Reagent grade sodium acetate and hydrochloric acid were used. Sodium acetate (27.3 gm) and hydrochloric acid (60 ml of 1 N) were combined and diluted to 1 liter.

Phthalate Buffer pH 6

Reagent grade potassium acid phthalate and reagent sodium hydroxide were used to prepare the buffer. Potassium acid phthalate (10.2 gm) and sodium hydroxide (1 gm) were dissolved and diluted to one liter.

CHAPTER IV

PRELIMINARY INVESTIGATIONS

For the majority of chelates the numerical values of the stability constants of the cadmium and zinc chelonates are very close. One remarkable exception is ethyleneglycol-bis(aminoethyl)-tetraacetic acid (EGTA). The absolute stability constants of the EGTA complexes of cadmium and zinc are 16.7 and 12.8 logarithmic units, respectively (see Table 1) (37). The difference of 3.9 logarithmic units would seem to provide a difference of sufficient magnitude to allow an amperometric titration. (For extrapolative techniques a difference of 2 logarithmic units in the stability constants represents about the minimum for a selective determination. A visual titration requires a difference of at least five logarithmic units.) It must be noted, however, that the stability constants quoted are the absolute stability constants. Consideration of the possible conditions for a titration must be made.

For the practical titration, an ammonia-ammonium chloride buffer of pH 10 might be chosen, with the total ammonia concentration ($[NH_3]$ + $[NH_4^+]$) of 0.1 M. Under these conditions (calculating as described earlier) the logarithms of the α_M-factors for cadmium and zinc are 3.1 and 4.7, respectively. The proton side reaction (α_Y-factor) affects the stabilities of both complexes equally, and at pH 10 is negligibly different from one. The conditional constants are calculated to be 13.6 and 8.1 for cadmium and zinc, respectively. Thus, under these conditions for the titration

Table 1. Logarithms of the Absolute and Apparent Stability Constants of the EGTA Complexes of Some Metal Ions and α_M Factors for 0.1 M and 1 M Total Ammonia ($[NH_3] + [NH_4^+]$).

Metal Ion	log K_{abs}	log α_M (pH 10, Total NH_3 0.1M)	log K_{app}	log α_M (pH 10, Total NH_3 1M)	log K_{app}
Cd^{+2}	16.7	3.1	13.6	6.8	9.9
Zn^{+2}	12.8	4.7	8.1	8.7	4.1
Cu^{+2}	17.8	8.3	9.5	12.2	5.6
Ba^{+2}	8.4	-	8.4	-	8.4
Ca^{+2}	11.0	-	11.0	-	11.0
Hg^{+2}	23.2	15.6	7.6	19.0	4.2
Mg^{+2}	5.4	-	5.4	-	5.4
Sr^{+2}	8.5	-	8.5	-	8.5
Mn^{+2}	12.3	-	12.3	-	12.3
Co^{+2}	12.3	2.0	10.3	5.4	6.9
Ni^{+2}	13.6	3.9	9.7	8.4	5.2
Pb^{+2}	14.6	-	14.6	-	14.6

the difference in the effective stability constants is 5.5 logarithmic units. An ammonia-ammonium chloride buffer also provides a high buffer capacity in a pH region where the proton competition reaction is not important as reflected in the near unity value for α_Y. The buffer also provides a complexing agent for cadmium and zinc which prevents their precipitation as hydroxides at high pH.

The difference of 5.5 logarithmic units would indicate the possibility of a visual titration, if a suitable indicator could be found. The possibility of finding an indicator which reacts selectively with cadmium in the presence of zinc seems remote. Another means of detecting the end point is thus needed.

Cadmium is known to give well defined polarographic reduction waves at the dropping mercury electrode (DME) in several supporting electrolytes. In an ammonia-ammonium chloride buffer, both cadmium and zinc exhibit well defined polarographic reduction waves. The half-wave potentials have been shown to be at -0.81 volts and -1.35 volts versus the saturated calomel electrode (SCE) for cadmium and zinc, respectively. This wide difference in half-wave potentials allows great leeway in the selection of a potential such that cadmium is selectively reduced. The linearity of the diffusion current with concentration has been verified over a wide range of concentrations. The diffusion current has been shown to be proportional to the cadmium concentration to better than 0.2 per cent over a 630-fold range of concentration (30). Based on calculations using equation 16, no direct interferences from the metal chelates formed during the titration are expected. The direct titration of cadmium with EGTA in the presence of zinc thus seems polarographically feasible, if the general

conditions for a chelometric titration with an amperometric end point can be met (see page 6).

In order to verify the theoretically deduced possibility of titrating cadmium with EGTA, several titrations were performed. A solution of cadmium (about 5×10^{-4} M) in 0.1 M ammonia buffer pH 10 and 0.1 M potassium nitrate supporting electrolyte was titrated with 0.01 M EGTA. The diffusion current was observed at an applied potential of -0.9 volts versus the SCE and plotted versus milliliters of titrant. The expected straight line decrease in diffusion current with titrant added was not observed. Rather, two lines of slightly different slope were observed, neither of which corresponded to the slope deduced from the known concentrations of cadmium and EGTA. See Figure 6. The first intersection was found not to be reproducible, but its value seemed to center about a value which was half of the second intersection.

The double slope was initially interpreted as a tendency of the EGTA chelon to form a complex containing two metal ions per chelon molecule. Some strength can be added to this premise by considerations of the structure of the chelate. EGTA is essentially a straight molecule with a chelating group at each end. In order to form a 1:1 complex, the molecule must be oriented such that both ends are bonded to the single metal cation. The likelihood of such an orientation decreases with an increase in the number of atoms separating the end groups. Careful standardization of stock cadmium and EGTA solutions virtually eliminated this explanation of the double slope.

Further investigations led to the discovery of a reduction wave at about -1.0 volts versus SCE. No attempts to assign this wave to the

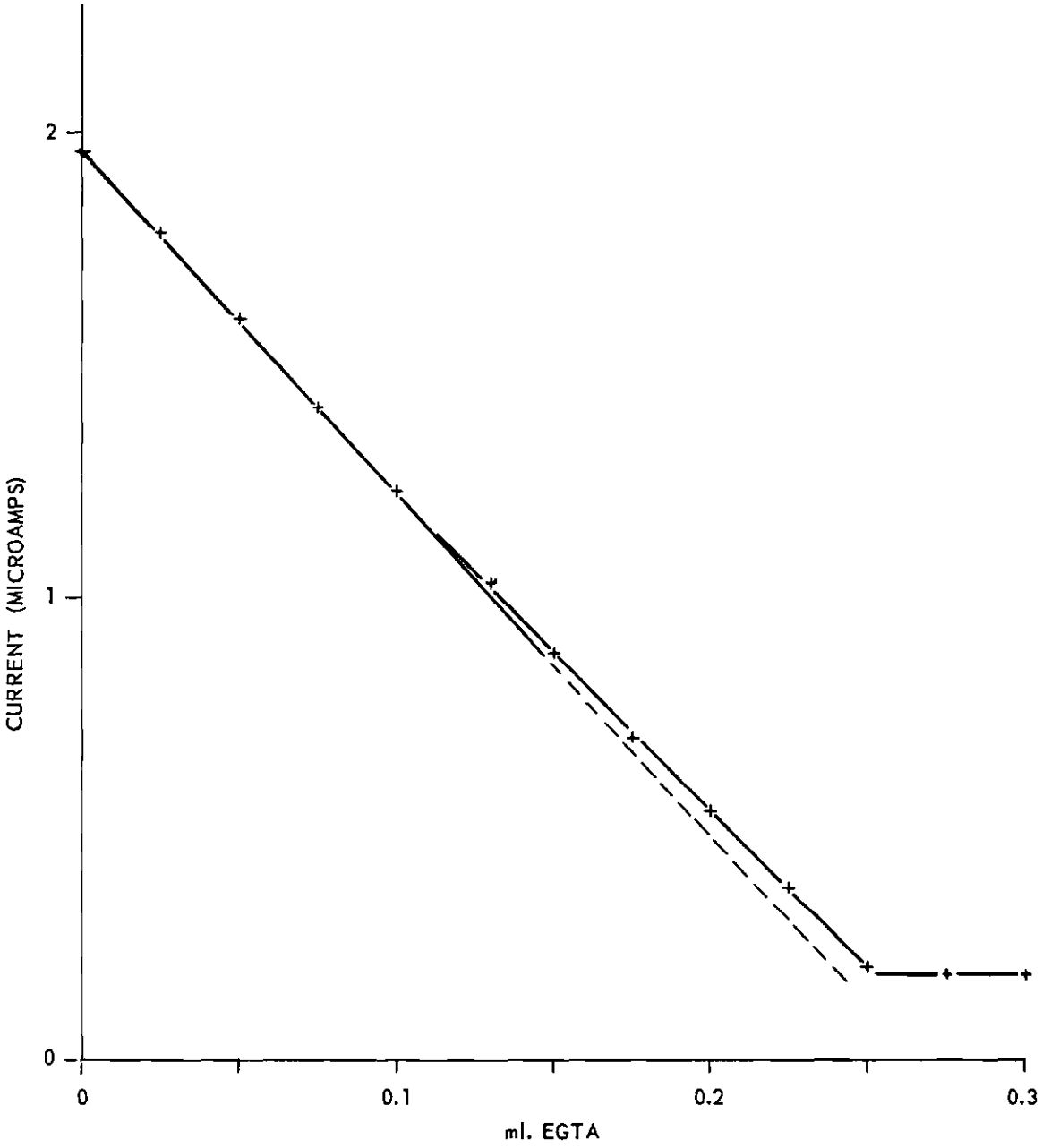

Figure 6. Double Slope Titration Curve of Cadmium (see text).

presence of an impurity were successful. The wave height was shown not to be proportional to the square root of the height of the mercury column associated with the dropping mercury electrode. This indicated a kinetically controlled wave. (A wave is said to be kinetically controlled when the limiting value of the current is dictated not by diffusion, but by a slower process such as dissociation on the electrode surface.)

In the amperometric titration of cadmium with ethylenediaminetetraacetic acid (EDTA), Tanaka, Oiwa and Kodawa (36) have reported the existence of a kinetically controlled reduction wave at about -1.0 volts versus the SCE. This wave has been described as the result of the reduction of cadmium freed by the dissociation of the cadmium-EDTA chelonate on the surface of the mercury drop electrode. A similar mechanism is here proposed to explain the wave observed in the cadmium-EGTA system. The cadmium-EGTA kinetic wave has been shown to be markedly dependent on the concentration of gelatine.

Tanaka, Oiwa, and Kodawa also noted that high results were obtained when cadmium was titrated with EDTA in the absence of gelatine. This was attributed to the increase in current due to the kinetic process. They report that this error in results was corrected when the kinetic wave was suppressed by the addition of gelatine. A tendency to high results in the cadmium-EGTA titration in the absence of gelatine was not observed at -0.9 volts. The maximum suppressing abilities of gelatine do, however, justify its use, and all reported titrations were performed in the presence of gelatine unless otherwise noted. That the kinetic wave here described is not a contributing factor in the formation of the unexpected break in the cadmium titration was shown by performing a titration in the presence of gelatine in sufficient amount to

suppress the kinetic wave. The shape of the titration curve was unaltered.

With no further hints as to the cause of the double slope available, a review of the routine assumptions was instigated. Two previously discounted factors were found to be involved in the mechanism of the double slope, the dilution error and the presence of dissolved oxygen. Each factor had been investigated individually and found clear of suspicion. Only elimination of all other logical explanations led the investigation back to find not a single cause, but two independent effects superimposed.

Dilution Correction

If one of the pair must be called the primary cause, this distinction should go to the dilution correction. It can be seen from equation 16 that the diffusion current is inversely proportional to the volume for a given quantity of an electro-reducible specie. Thus at any point in a titration the current measured, i_m, is dependent not only on the amount of the titrated specie not yet complexed, but is also dependent on the total volume of the solution. The total volume in the initial volume, V, plus the volume of the titrant added, v. If i_m is the measured diffusion current at a given point in the titration, the diffusion current, i_d, for the hypothetical no-dilution case is given below.

$$i_m = \frac{V}{V + v} \cdot i_d \qquad (18)$$

At any point in the titrations the difference between the measured current and the desired no-dilution current is $i_m - i_d$.

$$i_m - i_d = i_d \left[1 - \frac{V}{V + v} \right] \qquad (19)$$

Examination of equation 19 reveals that the deviation from i_d assumes an unexpected character due to the nature of the measurement. Near the start of the titration v is quite small compared to V so that the term within parentheses is not much different from zero, and the difference $i_m - i_d$ is near zero. Near the end point i_d becomes small and the difference $i_m - i_d$ once again approaches zero. Thus the deviations in measured diffusion currents due to dilution are of significance only away from the starting point and the end point. The deviations are further seen to be negative; that is, the measured current will appear as a curve concave downward with respect to the "no-dilution" curve. The maximum deviation is at the half-way point in the titration.

Proper interpretation of the curvature due to dilution was hampered by another deviation caused by dissolved oxygen. Oxygen constitutes one of the major interferences in polarographic investigations. The main contributing factor to the seriousness of the problem caused by its interference is the wide distribution in sample and reagent solutions. Oxygen shows in most supporting electrolytes two reduction waves, one occurring at about -0.05 volts and the second at -0.9 volts versus the SCE. Each of these waves shows high values for the diffusion current coefficient, that is, high diffusion currents as a function of concentration. Interference due to oxygen is generally eliminated by removing dissolved oxygen. This is standard polarographic practice and is usually accomplished by passing a polarographically inert gas through the solution

just prior to measuring the current. It is generally accepted that bubbling nitrogen through the solution via a sintered glass disk for five minutes will remove all but negligible quantities of oxygen (38). In an amperometric titration bubbling for one or two minutes after each addition of titrant removes oxygen introduced with the titrant. These periods were found insufficient in the amperometric titration of cadmium with EGTA. Too short de-aeration times were found to leave enough oxygen in solution to contribute significantly to the limiting current. Subsequent de-aeration periods after the addition of titrant resulted in a decrease in total dissolved oxygen. This effect led not only to a higher slope than expected for the titration curve, but to erratic results as well. Each titration curve was found to be the result of the decrease in current due to reduced oxygen concentration and the concave contribution of the dilution error both superimposed on the linear decrease in cadmium diffusion current. Elimination of either of the causes of the deviation without elimination of the other led to a curve which maintained a portion of the total deviation. Therefore, neither cause was initially suspected.

Oxygen

The nature of the interference of oxygen in polarographic investigations has been discussed above. The seriousness of the presence of oxygen in amperometric titrations is reduced by the variety of straightforward methods for its removal. Several of these were tried. The simplest, but not always the most feasible in practical analysis, is the displacement of dissolved oxygen by nitrogen, hydrogen, or some other polarographically inert gases. This is accomplished by bubbling the gas through the sample solution prior to the titration and after each

addition of titrant. This is a time consuming operation. In the application of this method to the amperometric titration of cadmium difficulties as described above were encountered if initial bubbling time was significantly less than fifteen minutes. The time required after each addition was found to be about five minutes. A further problem was encountered in ammonia solution since the nitrogen bubbling through the solution carried off ammonia, reducing its concentration in the sample solution. Despite these difficulties, this was the most frequently employed method of removing oxygen in this work, since the ammonia concentration was found to be not too critical.

Two methods of chemical reduction of oxygen were investigated. The addition of sodium sulfite is known to be effective in chemically reducing dissolved oxygen. The use of sulfite was tried and found to be effective in oxygen removal, but gave erratic results in the cadmium determination so its use was abandoned. Ascorbic acid was employed with great success for oxygen removal in the direct titration of cadmium. At low pH it was necessary to catalyze the "autoxidation of ascorbic acid". "A concentration of 2×10^{-5} moles per liter of copper increases the reaction rate by a factor of 10^4 (35)." This method of oxygen removal catalyzed by copper could not be extended to use in the amperometric indicator ion method described in Chapter V because at the high pH of the method ascorbic acid reduces copper as well as oxygen, thus removing the indicator from the solution.

Maximum Suppressors

One of the characteristics encountered in most polarographic investigations is the polarographic maximum. Maxima are anomalous

current rises occurring in general on top of polarographic reduction waves. The anomalous wave does not occur in the absence of any reducible substance and hence it cannot be corrected for by a blank. Several theories of maxima have been proposed, none yet completely explains the phenomenon.

The current practice in practical polarography is to limit the occurrence of maxima by the addition of maximum suppressors. These are generally surface active agents which have the property of completely eliminating the maxima even when present in very low concentrations. Three of the most popular among a vast number of maximum suppressors are Triton X-100, gelatine, and methyl red.

Triton X-100 and gelatine were employed in the amperometric titration of cadmium. Each functioned well in that no maxima were observed in their presence and no interference with the titration was found.

One new substance was investigated and can be added to the long list of maximum suppressors. General Electric Antifoam 60 was first employed to reduce foaming due to bubbling when Triton X-100 was used. It was soon found that Antifoam 60 acts as a maximum suppressor. This was tested and proved on maxima in copper solutions, about 5×10^{-3} volume per cent being sufficient for complete suppression of the maxima. Either Antifoam 60, gelatine, or both were used in all titrations.

The primary advantage of Antifoam 60 is the complete absence of foaming which constitutes a major problem with most surface active agents used as maximum suppressors. Relatively high amounts of Antifoam

are required which may in some cases be a drawback. This disadvantage is overcome by using Antifoam in conjunction with some surface active agent such as gelatine for maximum suppression.

CHAPTER V

EXPERIMENTAL

Two of the methods of applying amperometric end-point detection to chelometric titrations as described in Chapter II were applied to the cadmium-EGTA titration. Although the prime purpose of this investigation was the development of an amperometric indicator method to complement the previously mentioned photometric method, certain advantages of the direct titration justify its development.

Direct Titration

Preliminary investigations verified the theoretically deduced possibility of titrating cadmium. In order to determine the potential for the practical titration, the polarograms of the species concerned were compared. The predicted inert character of the cadmium and zinc chelonates was shown by recording polarograms of these species in 0.1 M ammonia buffer pH 10 in the presence of 0.002 per cent gelatine. The polarograms of cadmium and zinc were recorded in 0.1 M ammonia buffer pH 10 also. These polarograms are shown in Figure 7. A potential of -0.90 volts versus the SCE was selected.

Practical titrations of solutions containing known amounts of cadmium confirmed the practicability of the direct titration of cadmium. Each solution of known cadmium content also contained a known quantity of buffer pH 10, a

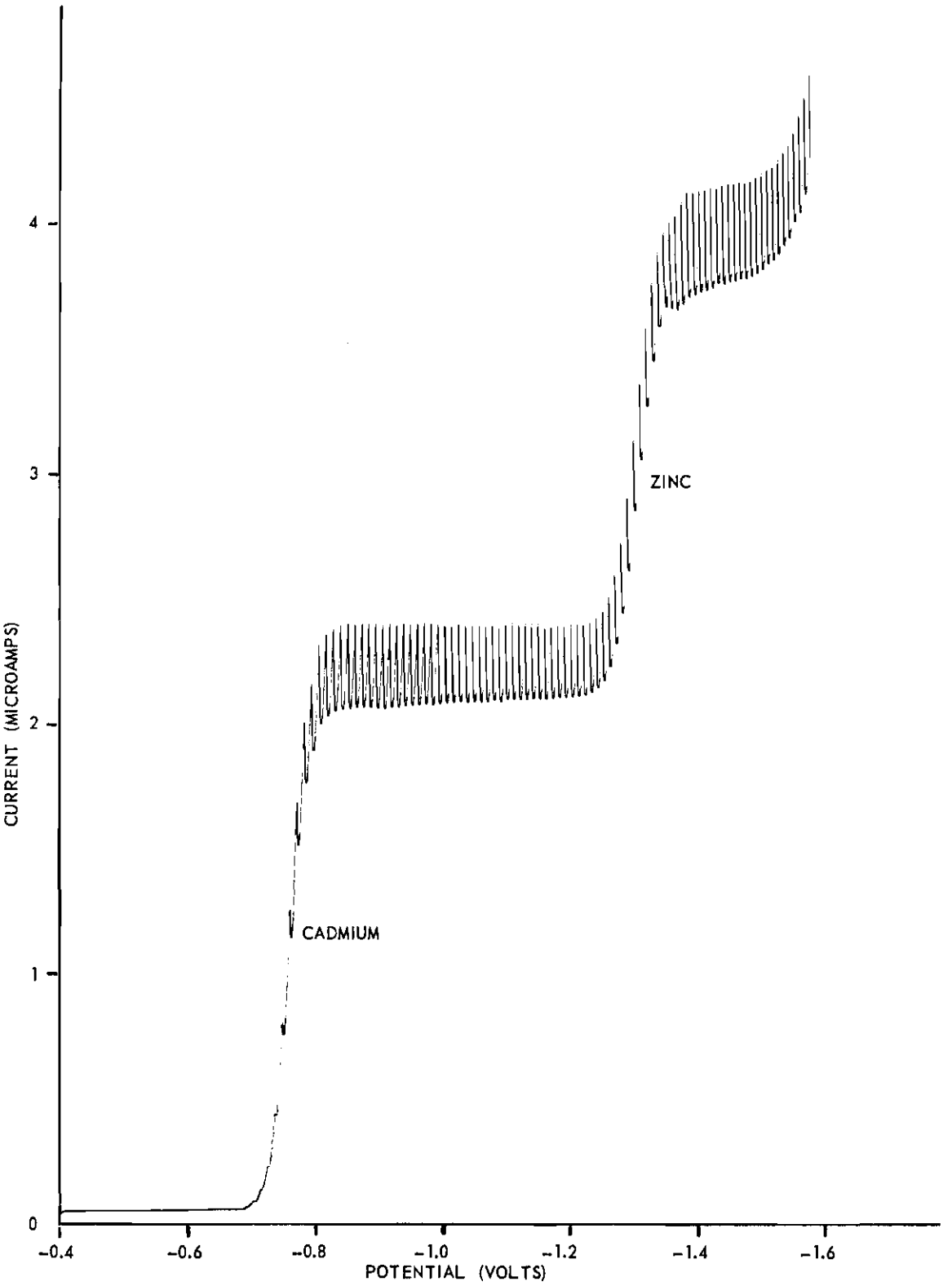

Figure 7. Polarograms of Cadmium and Zinc in Buffer pH 10.

maximum suppressor, and was 0.1 N in potassium nitrate or chloride as a supporting electrolyte. Some of the results of this series are shown in Table 2. A typical titration curve has been shown in Figure 3.

Unfortunately, many substances are reducible at the DME in buffer pH 10 at an applied potential of -0.90 volts versus SCE or less. One of these is oxygen, whose reduction wave appears at about -0.9 volts. In general, this type of interference is not fatal to the method if the concentration of the specie remains constant throughout the titration. Even when the specie remains constant, however, the sensitivity of the method is impaired. For this reason it is desirable to perform the titration at a lower potential, if possible.

It was found that a successful titration could be performed at a lower potential by choosing another buffer system. Both acetate buffer pH 5, and phthalate buffer pH 6 were used. In each case the solvated cations of cadmium and zinc are reducible at a potential less than that required for the relatively stable ammonia complexes. (See Table 1.) In addition, at these low pH values no tendency to precipitate hydroxides is observed. A series of titrations under these conditions were carried out at an applied potential of -0.7 volts versus the SCE, and some of the results recorded in Table 3. The potential for the titration was chosen after considering the polarograms of the cations under the proposed conditions for the titration. It was chosen to be at the low potential end of the diffusion current plateau resulting from the reduction of cadmium and to be below the start of the zinc reduction wave.

Table 2. Representative Results for the Direct Titration of Cadmium in Buffer pH 10.

Cadmium (meq.* x 10^2)		
Taken	Found	Δ
1.55	1.49	-0.06
1.92	1.90	-0.02
2.56	2.55	-0.01
2.89	2.91	+0.02
3.13	3.11	-0.02
3.49	3.49	0.0
4.00	4.00	0.0
4.80	4.81	+0.01
5.10	5.10	0.0
7.79	7.76	-0.03
8.14	8.16	+0.02
9.57	9.59	+0.02
10.46	10.47	+0.01

* meq. = milliequivalents

Table 3. Representative Results for the Direct Titration of Cadmium in Buffer 5 and Buffer 6.

Cadmium (mequiv. x 10^2)					
Acetate Buffer 5			Phthlate Buffer 6		
Taken	Found	Δ	Taken	Found	Δ
0.96	1.00	+0.04	4.07	4.09	+0.02
1.63	1.58	-0.05	4.07	4.10	+0.03
2.44	2.43	-0.01	5.10	5.10	0.0
4.07	4.06	-0.01	1.63	1.60	-0.03
14.49	14.59	+0.10			

Zinc

The effect of the presence of zinc on the determination of cadmium was investigated next. This was done by titrating solutions of known cadmium concentration after the addition of zinc. The presence of large proportions of zinc was found to have no influence on the location of the end point. Satisfactory results were obtained in solutions with a cadmium to zinc ratio of up to 1:500. Each of the buffers previously proved for cadmium alone was tried and shown to initiate no zinc interferences. Some of the results of this series of titrations are found in Table 4.

Interferences

The effect of the presence of cations other than zinc on the cadmium titration was evaluated by titrating known quantities of cadmium in solutions containing the various cations. Most of these ions which were shown not to interfere with the photometric method of Flaschka and Ganchoff (1) - Iron(II), Cobalt(II), Nickel(II), Aluminum(III), and the alkali metals - do not interfere with the amperometric method. The usefulness of the amperometric method lies with those metals whose interference in the photometric method is overcome by the amperometric method. These will now be discussed.

Calcium and magnesium do not interfere if conditions are carefully controlled. In fact, solutions with up to a 100-fold excess of calcium over cadmium have been titrated with excellent results if the ammonia concentration is kept low. The dependence on the ammonia concentration is readily seen from a consideration of the α_M factor. The ammonia concentration has no effect on the stability constant of calcium which is 10^{11}. On the other hand α_M for cadmium in a 1 M ammonia solution reduces

Table 4. Titration of Cadmium in the Presence of Zinc. Representative Results.

Cadmium (mequiv. x 10^2				
Taken	Found	Δ	Buffer	Cd:Zn
4.07	4.09	+0.02	Ammonia 10	1:1
5.10	5.12	+0.02	Ammonia 10	1:100
2.55	2.56	+0.01	Ammonia 10	1:10
5.10	5.10	0.0	Ammonia 10	1:10
5.10	5.05	-0.05	Acetate 5	1:10
4.80	4.78	-0.02	Acetate 5	1:10
2.44	2.43	-0.01	Acetate 5	1:100
5.10	5.10	0.0	Phthlate 6	1:1
5.10	5.11	+0.01	Phthlate 6	1:5
5.10	5.03	-0.07	Phthlate 6	1:10
5.10	5.10	0.0	Phthlate 6	1:20

the effective stability constant from the absolute value of $10^{17.8}$ to $10^{11.0}$ at pH 10. Thus in a 1 M ammonia solution calcium and cadmium are cotitrated. In order to maintain a difference in conditional constants of at least two logarithmic units the total ammonia concentration should not exceed 0.4 M. Magnesium, barium, and strontium are seen to behave in a similar manner.

The strong dependence of K_{eff} on the ammonia concentration for cadmium also allows the titration of calcium in solutions of high ammonia concentration. In this titration K_{eff} for cadmium is very much lowered by adding large quantities of ammonia. Calcium is then selectively titrated first. Cadmium is not titrated until after the calcium end point. The disappearance of the cadmium past the calcium end point serves as an amperometric indicator. (See page 1.) The cadmium end point is then determined directly as before. Good results were obtained by this method so long as the calcium and cadmium concentrations were comparable. Further development of this method for calcium is in progress.

Iron(III) interferes with the titration both by competing with cadmium for the available chelon and by its electroactivity at the DME at low potentials. This interference was avoided by converting Fe(III) to Fe(II) with ascorbic acid in acidic solution. After the reduction the pH was adjusted to about 5 and the titration carried out at -0.7 volts versus the SCE. The resultant solution is occasionally dark, evidently due to the presence of mixed oxidation states. This coloration would interfere with the photometric titration. Results for amperometric method were satisfactory up to about 20:1 iron to cadmium. Above this ratio the curvature at the end point becomes pronounced.

Results for a variety of titrations involving interfering ions are shown in Table 5.

Lead(II), Copper(II), Tin(II), and Cobalt(II) among others interfere. In most cases the problem of these ions is serious because theseparation of cadmium and zinc from most other elements can be effected by ion exchange methods (32) or by solvent extraction techniques (14).

Procedure. When titrating cadmium by the direct method, the following procedure was used. The sample containing cadmium and zinc is dissolved and an aliquot pipetted into the titration cell. Three milliliters of Buffer 10 are added. Ten milliliters of 1 M potassium nitrate are added as supporting electrolyte. Gelatine, 0.01 per cent, is added as maximum suppressor, and the solution is diluted to about 100 ml. with de-ionized water. The cell assembly (Figure 6) is now introduced into the cell. Oxygen is next removed by one of the methods discussed in Chapter IV, generally by passing a nitrogen stream through the solution for fifteen minutes. The solution is then titrated with EGTA bubbling nitrogen after each addition. The diffusion current is recorded at the potential dictated by the buffer used (-0.90 volts) and plotted versus milliliters of (0.1000 M) EGTA. For small quantities a smaller cell and cell assembly may be used.

Amperometric Indicator Titration

The desirability of performing an amperometric titration at as low an applied potential as possible has been previously noted. At a low potential fewer ions will be electro-active at the DME and interferences of this nature will be minimized. The use of copper as an

Table 5. Titration of Cadmium in the Presence of Calcium, Magnesium, and Iron(III).

Cadmium meq. x 10^2					
Taken	Found	Δ	Interfering Ion	Ratio to Cadmium	Buffer*
1,92	1.90	-0.02	Ca	1:1	B-10
1.92	1.90	-0.02	Ca	50:1	B-10
1.92	1.95	+0.03	Ca	100:1	B-10
4.80	4.81	+0.01	Cal	1:1	B-10
4.80	4.86	+0.06	Ca	10:1	B-10
5.10	5.12	+0.02	Mg	10:1	B-10
5.10	5.11	+0.01	Mg	16:1	B-10
5.10	5.08	-0.02	Mg	100:1	B-10
4.80	4.79	-0.01	Fe	1:1	AB-5
4.80	4.79	-0.01	Fe	10:1	AB-5
4.80	4.70	-0.10	Fe	10:1	AB-5
4.80	4.88	+0.08	Fe	100:1	AB-5
1.98	2.02	+0.14	Ca	1:2	B-10h
1.92	1.93	+0.01	Ca	1:1	B-10h
3.12	3.10	-0 02	Ca	1:1	B-10h
1.45	1.37	-0.08	Ba	20:1	B-10
1.59	1.59	0.0	Ba	50:1	B-10

* B-10 indicates ammonia-ammonium chloride buffer pH 10. approx. 0.1 M;
B-10h indicates a much higher concentration of B-10
AB-5 indicates an acetate buffer of pH 5.

amperometric indicator provides a method of performing the titration of cadmium at a low applied potential.

Because of the difference of 5.5 logarithmic units in the apparent stability constants of the cadmium and zinc EGTA chelonates in ammonia buffer pH 10, the possibility of placing a self-indicating system between the cadmium and zinc was considered. The requirements which must be fulfilled are that the difference in apparent stability constants of the cadmium and the amperometric indicator ion chelonates be of sufficient magnitude to allow end-point detection. (It has been previously noted that this difference must be at least two logarithmic units.) Further, the zinc-EGTA chelonate apparent stability constant should be no lower than that of the amperometric indicator system. Copper is particularly well suited for this purpose.

At the time of the start of this investigation no value for the copper EGTA chelonate stability constant was available. From the shift in half-wave potentials of the chelonate from that of the uncomplexed copper, this constant was estimated to have a value of about 17.6 for the logarithm of the absolute stability constant (see Appendix). Reilly has since published a value of 17.8 (34).

Comparison of the apparent stability constants at pH 10 in 0.1 M total ammonia concentration shows the order of the effective stability constants to be $Cd > Cu \geq Zn$. The cadmium constant is larger than that of copper by about four logarithmic units which means that cadmium is titrated before copper with EGTA in the presence of this concentration of buffer. The difference is seen to be of sufficient magnitude to allow amperometric end-point detection.

The slope of the curve after the end point is dependent on the concentration of ammonia. This portion of the titration curve corresponds to the titration of copper. It can be seen from consideration of α_M that as the ammonia concentration increases, K_{eff} for the copper EGTA chelonate decreases. Thus a small slope and large curvature due to dissociation of the copper-EGTA chelonate are seen for high ammonia concentrations. The slope will also be reduced by the presence of cations such as barium(II) and strontium(II) whose apparent stability constants are comparable to the copper EGTA apparent stability constant. The effect on the slope is due to cotitration.

In order to establish the potential at which copper might be used as a slope indicator, polarograms of copper under the proposed conditions of the titrations were recorded (Figure 7). In choosing a potential two factors were considered. It was desirable to choose as low a potential as practicable in order to exclude as many potential interferences as possible. On the other hand, the potential chosen was required to be high enough to reduce copper and to give a diffusion current of sufficient magnitude to detect copper present in very low concentrations. In addition, it was desirable to choose a potential on a diffusion plateau so that small variations in the applied potential would not be significant. As can be seen in Figure 7, copper in ammoniacal media is reduced in two steps. The first corresponds to a one-electron reduction to copper(I), the second a one-electron reduction to copper (0). The plateau associated with the first step of the reduction was selected for the amperometric indicator titration. The titrations were carried out at -0.30 volts.

The theoretically deduced conditions for the titrations were verified by titrating solutions of known cadmium content. Some typical results are shown in Table 6.

At the potential used in this amperometric titration only the first reduction wave of oxygen (-0.05 volts) is in evidence and, if there is no drastic change in the oxygen concentration, gives a constant diffusion current. Based on the assumption of constant oxygen diffusion current, the cadmium titration was carried out as before without prior removal of oxygen. Typical results are recorded in Table 5. In general, it was found that for this method satisfactory sensitivity and excellent accuracy could be obtained in the presence of oxygen.

Zinc. The effect of the presence of zinc on the determination of cadmium was next investigated by titrating solutions of known composition. It was found, as shown by representative data in Table 7, that zinc does not interfere in amounts up to a 500-fold excess over cadmium.

Interferences

The influence of other metal ions on the titration was next investigated. Iron(II), cobalt(II), magnesium(II), and nickel(II) were found not to interfere. Since the apparent stability constants for lead and calcium under the conditions of the titrations are greater than that for copper, these two are cotitrated. Nickel(II) and cobalt(II) are cotitrated with copper after the cadmium end point. This decreases the slope of the indicator line, but does not alter the cadmium result.

The masking of iron(III) by reduction as in the direct method, could not be used since ascorbic acid reduces copper(II). The masking of limited amounts of iron(III) was accomplished, however, by the

Table 6. Results of Titrating Cadmium by the Amperometric Indicator Method.

Cadmium meq. x 10^2			
Taken	Found		Δ
1.06	1.06		0.0
3.18	3.15		-0.03
4.24	4.22		-0.02
5.30	5.30		0.0
8.49	8.54		+0.05
5.30	5.28		-0.02
5.30	5.29	O_2not removed	-0.01

Table 7. Effect of Zinc on the Amperometric Indicator Titration of Cadmium.

Cadmium meq. x 10^2			Zinc
Taken	Found	Δ	Ratio to Cd
5.30	5.32	+0.02	1:1
5.30	5.30	0.0	2:1
5.30	5.28	-0.02	4:1
5.30	5.34	+0.04	10:1
5.30	5.26	-0.06	40:1
5.30	2.08	+0.05	500:1

use of lactate or tartrate. The upper limit for this type of masking was found to occur at iron concentrations above about 0.01 M. Above this for either masking agent, turbidity was observed which did not interfere directly; however, coprecipitation and irregularity due to adsorption on the mercury drop electrode began to affect the results. Representative results appear in Table 8. Similar results were obtained with aluminum(III).

Since the apparent stability constants of lead(II) and calcium(II) are significantly higher than that of copper under the conditions of the titration, these ions are cotitrated with cadmium. Magnesium(II), however, does not interfere in amounts up to about 20:1 compared to cadmium.

Procedure

The general procedure used when performing a titration is given here. The sample containing cadmium and zinc is dissolved and an aliquot is pipetted into the titration cell. Copper is added if not already present. Three milliliters of Buffer 10 were added. Ten milliliters of 1 M potassium nitrate are added as supporting electrolyte. Gelatine is added as maximum suppressor, 0.01 per cent, and the solution is diluted to about 100 ml with de-ionized water. The cell assembly (Figure 6) is introduced into the cell, and the titration with EGTA carried out at -0.30 volts as described for the direct method.

Table 8. Results of Titrations of Cadmium in the Presence of Iron(III).

Cadmium meq. x 10^2			Iron(III)	
Taken	Found	Δ	Ratio to Cadmium	
5.30	5.31	+0.01	2:5	Lactate
5.30	5.31	+0.01	3:5	
5.30	5.24	-0.06	1:5	
5.30	5.25	-0.05	1:5	
5.30	5.31	+0.01	1:1	Tartrate
5.30	5.30	0.0	1:2	

CHAPTER VI

DISCUSSION

It has been shown that cadmium can be successfully titrated in the presence of large quantities of zinc with EGTA, using an amperometric end-point detection. The titration can be carried out directly or an amperometric indicator can be used. The formation of ammonia complexes and of copper causes the apparent stability constant of copper-EGTA to have a value less than that of the cadmium-EGTA complex. Thus in ammonia buffer copper can function as the amperometric indicator ion.

Comparison of the two methods here developed is closely related to the consideration of interferences. The methods will therefore be discussed by consideration of the effect of various interferences on the determination. In order to be complete, the photometric method (1) whose limitations led to this investigation will be discussed here, also.

The common virtue of each of the three methods here considered is their insensitivity to large quantities of zinc in the sample solution. In fact, it has been shown that for determinations in ammoniacal media of cadmium in solutions containing up to a 500-fold excess of zinc, results are quite satisfactory. Some difficulty is expected and actually observed in titrations carried out in other media. The extremely favorable effect of the values of the α_M coefficients on the apparent stability

constants is responsible for the larger tolerance for zinc in ammoniacal solutions.

Iron and aluminum in the ammoniacal solution of the photometric titration are precipitated as the hydroxides. The precipitate interferes directly with the photometric determination. Moderate amounts of iron and aluminum can be masked by the addition of tartrate. In the amperometric indicator method the same precipitation of iron and aluminum is is observed. The limit of the amount which may be present without interference with the determination is, in this case, not the first appearance of a precipitate. In fact, the presence of a precipitate has no direct effect on the end point mechanism. When large amounts of iron or aluminum are present, however, coprecipitation may reduce the cadmium available for titration yielding low values for the end point. Tartrate and lactate were effectively used to extend the tolerable range of concentrations of iron and aluminum. An elegant possibility of excluding the interference of iron is the addition of ascorbic acid. When ascorbic acid is added to the acidic sample solution, iron(III) is reduced to iron(II). The solution can then be brought to the desired pH, buffer added and the titration of cadmium performed. This method also removes the troublesome dissolved oxygen by chemical reduction. This method of masking for iron cannot be used for the amperometric-indicator method since copper is also reduced under these conditions.

In the photometric procedure calcium was found to be cotitrated with cadmium. This is also the case in the amperometric-indicator method. By proper control of the ammonia concentration the relationship between

the effective stability constants of the cadmium and calcium EGTA complexes can be adjusted to allow titration of either or both. Cadmium can be selectively titrated at low ammonia concentrations where the effective stability constant relationship is Cd > Ca. In high ammonia concentration the effective stability constants are in the inverse order and calcium can be selectively titrated. In approximately 1 M ammonia are cotitrated. Barium, strontium and magnesium behave in a similar manner. Their stability constants are, however, lower and as a result the concentration tolerances are higher.

The metal most frequently accompanying cadmium and zinc is lead and unfortunately it is always cotitrated with cadmium. However, there is the possibility of titrating lead in another aliquot in which cadmium and zinc have been masked by cyanide. Cadmium can then be obtained from the amperometrically determined sum of cadmium plus lead.

Oxygen is an interference only in the amperometric methods. Its removal is usually required in all cases with the exception of the amperometric-indicator method. In this case the current background due to dissolved oxygen does not significantly reduce the sensitivity of the determination since at the potential of this determination only the first reduction wave of oxygen is observed.

The occurrence of many other metal ion impurities in practical samples is likely. The effect of these impurities on the titration of cadmium can be best decided by considering the stability constant of the metal under the conditions of the titration. A systematic study of possible interferences will reveal a large number of ions which do interfere. Almost without exception cadmium and zinc together can be separated

from these by extraction techniques or by ion exchange.

APPENDIX

Copper-EGTA Stability Constant

At the time of the start of this investigation no value for the copper-EGTA stability constant was available. It was desirable to have a vlue of this constant to be used for the mathematical evaluation of the conditions for proposed titrations. The stability constant was estimated from the difference in the half-wave potential of complexed and uncomplexed copper.

In aqueous solution copper(II) is reduced in one step at a potential of +0.017 volts versus SCE.

$$2e^- + Cu^{++} \rightarrow Cu^{o}(Hg) \qquad (18)$$

where Cu(Hg) indicates the final form of the copper as an amalgam. In the presence of EGTA the electrode reaction becomes

$$CuY^{=} + 2H^{+} + 2e^- \rightleftarrows Cu^{o}(Hg) + H_2Y^{=} \qquad (19)$$

the final form of the chelon being pH dependent. It is convenient to consider this reaction as the sum of two partial reactions:

$$2H^{+} + CuY^{=} \rightleftarrows Cu^{++} + H_2Y^{=} \qquad (20)$$

and

$$Cu^{++} + 2e^- \rightleftarrows Cu^{o}(Hg) \qquad (21)$$

This does not imply a mechanism for the net reaction nor is it

necessary for deriving the expressions below. Reaction (21) is identical with reaction (18). Thus, the difference between the electrode process in the presence of EGTA and the process involving only the simple metal cations is reaction (20). The difference in half-wave potentials may be written as

$$E_{1/2)c} - E_{1/2)s} = \frac{0.0591}{n} \log K_{eff} - \frac{0.0591}{n} p \log C_Y \qquad (22)$$

and where effective the symbols are as used before. (See page 1.)

The effective stability constant for the copper-EGTA complex was estimated from the half-wave potentials of copper solutions, containing known concentrations of EGTA. Its concentration was varied over a reasonable range while maintaining the pH constant. The pH was controlled by the presence of ammonia buffer pH 10. As previously discussed, the value of the stability constant obtained under these conditions can be related to the absolute constant by application of the appropriate alpha factors. (See Chapter II.)

For a solution as described above in which the buffer concentrations ($[NH_3] + [NH_4^+]$) was 0.1 M and C_Y was 0.25F, the half-wave potential for the reduction of the complex was found to be -0.569 volts versus the SCE. This corresponds to a shift of -0.586 volts. From the above equation (22) with n = 2 and p = 1 we find that $K_{eff} = 9.2$. Application of the α_M factor for copper in ammonia (0.1M) solution (see Table 1), yields the value of the absolute constant K = 17.5 as an average of several measurements. Considering that no effort was made to control ionic strength and temperature, this agrees favorably with the value of 17.8 reported by Reilley (34).

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